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Borate Zirconia an Efficient Catalyst for The Synthesis of β -Enaminones in Aqueous Media

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ABSTRACT

An efficient synthesis of β -enaminone derivatives from dimedone and aromatic amines at room temperature using borate zirconia catalyst in aqueous media. Borate zirconia found to be efficient catalyst, experimental procedure is simple, reaction time is shorter and yield of the product is excellent.

Keywords: β -Enaminone, Amines, Dimedone, Borate zirconia

INTRODUCTION

β -enaminones is used as main intermediates in the synthesis of different heterocycles, in pharmaceuticals, naturally occurring alkaloids and as synthetic building block of a great variety of heterocycles [1-5]. However, the significance of β -enaminones as valuable biologically active compounds, their synthesis has received great attention of researchers and hence various methods have been recently reported such as Erabium (III) triflate [6], Ytterbium triflate [7], P_2O_5/SiO_2 [8], Cu-nanoparticles [9], heteropoly acid [10], $CeCl_3$ [11], AcOH [12], $HClO_4-SiO_2$ [13], montmorillonite K_{10} [14], silica gel [15], ceric ammonium nitrate [16], $CoCl_2 \cdot 6H_2O$ [17], $NaAuCl_4$ [18] $ZrCl_4$ [19] and I_2 [20]. Recently, β -enaminones synthesized by using Nano- SiO_2 [21], $NbOPO_4$ [22] and industrial quality graphene oxide [23]. However, our prime interest to develop new method for the synthesis of desired organic compounds. Here in we have developed simple and clean method for the synthesis of β -enaminone derivatives in aqueous media using solid borate zirconia catalyst.

Breslow et al. [24,25] studied on Diels-Alder reactions in aqueous media. The advantages of this reaction such as rate enhancement, insolubility of the final products, which facilitates their isolation by simple filtration. Synthesis of bioactive heterocyclic compounds in aqueous media is acting as a stepping stone in the greener synthesis in the context of green chemistry. Recently, the development of water-tolerant catalysts has rapidly become an area of intense research.

Boron oxide supported on zirconium oxide containing 30% of boron has been reported as a super acid catalyst for the decomposition of ethanol to ethylene [26], selective synthesis of ϵ -caprolactum [27,28], Friedel Craft benzoylation [29], selective C-methylation [30].

MATERIALS AND METHODS

General procedure: synthesis of β -enaminones

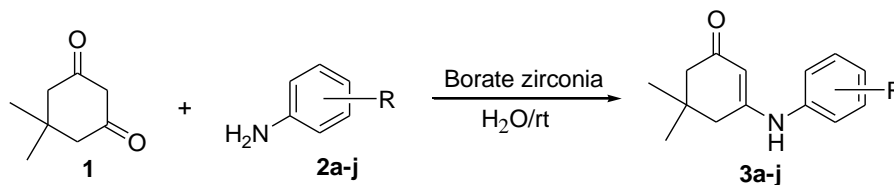
A reaction mass of dimedone 1 (1 mmol), aromatic amines 2a-j (1 mmol) and borate zirconia (10 mol%) were taken in a round bottom flask containing 5 ml of water. The reaction mass was stirred at room temperature for a stipulated time. The progress of reaction was monitored on TLC. After completion of the reaction, the mixture were diluted with cold water (10 ml), stirred for 5 min., and the resulting solid product was filtered, dried and crystallized in aqueous ethanol.

RESULTS AND DISCUSSION

In continuation of our work on development of simple synthetic methodologies [31-40], herein we report a simple and efficient synthesis of β -enaminone derivatives by the condensation reaction of dimedone and substituted aromatic amines in water at room temperature catalyzed by solid borate zirconia has been reported (Scheme 1).

To optimize the reaction conditions, initially, we have selected dimedone 1 and aniline 2a as standard model reaction. Firstly, the reaction were carried out in water in the absence of borate zirconia, product could not be detected at room temperature and reflux temperature even after 3 h (compound 3a). To firmly decide the optimal catalyst loading required, the reaction were reoccurred with varying amounts of borate zirconia (Table 1).

An excellent yield of 92% was obtained with 10 mol% of borate zirconia at room temperature in water within 40 min. In addition to increase in catalyst loading 15% or 20% did not have any significant effect on the yield of product. Whereas, decreasing the amount of catalyst, decreased yields (Entry 1-3 and Table 1).



Scheme 1: Synthesis of β -enaminone derivatives catalyzed by borate zirconia/ H_2O

Table 1: Molar ratio of catalyst for the model reaction

Entry	Mole%	Yield% ^a
01	00	--
02	02	55
03	05	70
04	10	92
05	15	92
06	20	90

Note: ^aIsolated yield of the product

With this surprising result, the method was continuing for a number of aromatic amines to research its scope and generality. Aromatic amines, including those containing electron-withdrawing groups (Such as Cl, F and Br) or electron donating groups (Such as CH_3 , OCH_3) were treated with dimedone catalyzed by borate zirconia at room temperature in water. The corresponding β -enaminone derivatives (3a-j) were formed with excellent yields within shorter reaction times and confirmed by IR, ¹H-NMR, Mass spectroscopic analysis. The results are summarized in Table 2.

Table 2: Borate zirconia catalyzed synthesis of β -enaminone derivatives

Entry ^a	R	Time (min)	Yield (%)	Melting point (°C)
3a	H	3 h at r.t.	-	-
3a	H	3 h at reflux	-	-
3a	H	60	92	181-183
3b	4-Cl	50	90	150-152
3c	4-OMe	40	92	104-106
3d	2,3-Cl	50	87	199-201
3e	2-Me	40	89	135-137
3f	3-Me	40	90	140-142
3g	4-Br	40	90	163-165
3h	4-Me	40	90	142-144
3i	3-OMe,4-OH	35	92	114-116
3j	4-F	50	88	192-194

Note: ^aIsolated yield of the product

CONCLUSION

In conclusion, we have developed simple and practical procedure for the synthesis of β -enaminone derivatives at room temperature in the presence of borate zirconia as a solid catalyst. The main advantages offered by the method are, mild reaction conditions, use of safer and ecofriendly catalysts and excellent yielding strategy.

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